Experimental and theoretical studies of perceptible color fading of decorative paints consisting of mixed pigments

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ABSTRACT

We study the color fading of paints films composed of mixtures of white rutile titanium dioxide and yellow arylide pigments dispersed in two polymer binders at different volume concentrations. The samples were exposed to ultraviolet radiations in an accelerated weathering tester during three weeks. The measured patterns in color variations appeared to be independent of the chemistry of the binders. We then developed a theoretical framework, based on the Radiative transfer Equation of light and the One Particle T-Matrix formalism to simulate the color fading process. The loss of color is correlated to the progressive decrease of the original colored pigment volume-filling fraction as the destructive UV radiations penetrate deeper into the films. The calculated patterns of color variations of paints film composed by mixtures of white pigments with yellow Cadmium Sulfate (CdS) and red Cerium Sulfide (Ce_2S_3) pigments showed the same trend as that seen experimentally.

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1. Introduction

Water based coatings are colloidal systems composed of mineral and organic particles of distinctive sizes and shapes, dispersed at different volume concentrations into a polymeric resin. They also include small quantities of specific chemical species (referred to additives) whose function is to enhance the paint properties such as foam control, flow, leveling and rheology. The resin is used as a binder to provide uniformity and mechanical coherence to the film in its dried state. The color of coatings is generated by addition of pigments, which can selectively absorb light in the visible spectrum. In the Decorative Paints business, color fastness represents the capacity of a given paint to maintain its original color over the time when exposed to environmental conditions such as solar UV radiation and chemical attack [1]. In producing high quality, long lasting paints it is necessary to minimize color fading in order to ensure customer satisfaction and thus commercial success. Color fastness is evaluated by measuring the magnitude of the color changes over the time. Usually, in addition to real world testing, evaluations of color fastness are performed in the laboratory using accelerated weathering testers that are specifically designed to simulate a wide range of UV, temperature and humidity conditions.

Color loss in paints can be as a result of binder degradation (leading to 'chalking' and whitening) or chemical degradation of

the color pigments, either by direct photolysis of the bonds by short wavelength UV radiation, or via secondary oxidative or reductive processes mediated by molecules present in the environment (such as oxygen or other pollutants), or generated by components of the paint itself (such as those produced by photo-activation of titanium dioxide pigment [2]).

There are several strategies to delay, or when possible, to prevent color loss. The first one consists of discarding the use of pigments that are highly sensitive to UV excitation. This can complicate the work of the formulator, who then needs to find an alternative pigment with same hue that does not alter the other performances of the paints. The second approach resides in controlling the photo activity of the particles by adding a surface treatment, usually composed of silica, alumina or zirconia, to traps the electron-hole pairs, created by the UV excitation, before they migrate at the pigment/binder interface. The third approach consists of limiting the penetration of the UV radiation into the film. This is achieved by adding protective organic molecules or inorganic particles that absorb and/or backscatter the destructive radiations before they irreversibly damage the pigments and the binder. In such case, the addition of surface treated rutile titanium dioxide pigments is convenient for at least three reasons: (a) They intrinsically strongly absorb and scatter UV radiation; (b) They are already present as opacifiers in the white bases used to formulate colored paints (c) They do not modify the hue of the original color. The last method consists of synthetizing and using polymer binders that are less sensitive to UV radiations.

It may seem intuitively obvious that the higher the percentage

of color pigment degraded in the film, the greater the color change that will result. However this is not true when there are mixtures of pigments present. In this case what is important is not the total amount of pigment degraded, but rather the total amount of perceptible pigment, which is a complex function of the optical properties of the pigment mixture. A better comprehension of those relations could improve colorfastness performance by allowing a better selection of raw materials. Therefore, the aim of this work is twofold: (a) To study the variations in color of paint films consisting of mixed pigments at different volume filling fraction. (b) To present and validate an original theoretical framework we have elaborated to simulate the color fading process in order to provide the basis of a mechanistic understanding of the origin of the perceptible color changes.

To carry out these objectives, the article is structured in two parts. In the first part we present and discuss color-fading measurements conducted at AkzoNobel Decorative Paints R&D laboratory on paint films that were exposed to an accelerated weathering tester. The second part is dedicated to the theoretical study. We first describe in details the modeling procedure that we implemented to simulate the loss of color then we present and discuss the results of our calculations. We finish by comparing the predictions of our model with the set of experimental data.

2. Experimental study

2.1. Composition of the paint films

The paints are composed of mixtures of white and yellow pigments at different volume fractions noted ϕ_W^0 and ϕ_Y^0 respectively (see Table 1). Each of the 63 mixtures was dispersed with the adequate package of additives in two polymeric binders having two different degradation rates: a vinyl acrylic latex and an acrylic latex noted P_E and P_R respectively. The white pigment, Ti-pure™ R-746 (rutile titanium dioxide), is designed to deliver high gloss and high durability while the yellow pigment, Yellow-74, is an organic pigment from the Arylide family.

2.2. Preparation of the samples

Films were drawn down under ambient conditions on a white plastic substrate using a spreading bar. The gap thickness was chosen to give a final dry film thickness of 75 μm. The latter was determined gravimetrically based in the known densities of the paint components and the area of the drawn down film. The samples were then conditioned in a dark incubator at 40 °C for 1 week in order to ensure that residual water and volatiles were removed. Once conditioned, the panels were cut to a size suitable for mounting in the accelerated weathering chamber.

Table 1
White and Yellow Pigment Volume Concentrations (PVC) utilized in the different samples.

PVC numbering	White ϕ_W^0 (unitless)	Yellow PVC ϕ_C^0 (unitless)
1	0.0	1.00×10^{-3}
2	3.00×10^{-3}	2.00×10^{-3}
3	6.00×10^{-2}	5.00×10^{-3}
4	9.00×10^{-2}	6.66×10^{-3}
5	1.50×10^{-1}	1.00×10^{-2}
6	2.50×10^{-1}	2.00×10^{-2}
7	4.00×10^{-1}	3.33×10^{-2}
8		5.00×10^{-2}
9		1.00×10^{-1}

2.3. Data acquisition

The following procedure is an internal test based on a modification of the procedure used by the US consumer Union testing house. The panels were place inside a Q-lab QUV/se UV test chamber fitted with UV340 bulbs and exposed to UV radiation at 0.44 W/m² without spray or condensation cycles for a period of 600 h. Panels were removed periodically (at least once per 100 h) and equilibrated in a controlled temperature of 23 ± 2 °C and humidity laboratory of $50 \pm 5\%$ for a few hours before being spectrophotometrically measured. The measurements were conducted on a Datacolour 600, gloss excluded configuration, from 0.4 to 0.7 micrometers at an interval of 0.01 μm. For each of the samples, a measurement of the diffuse reflectance was also conducted at t=0 (before UV irradiation had commenced). Spectra were then converted into CIELAB color space coordinates referred to as the CIE 1976 (L^*,a^*,b^*) color coordinates [3], where CIE stands for Commission Internationale de L'Éclairage (International Commission on Illumination). We then calculated the color differences ΔE, defined as the Euclidean distance between the CIELAB coordinates of the paint of reference and the paint film into consideration, via the relation:

$$\Delta E = \sqrt{\left(L^{*,R} - L^* \right)^2 + \left(a^{*,R} - a^* \right)^2 + \left(b^{*,R} - b^* \right)^2} \tag{1}$$

Where ($L^{*,R}$,$a^{*,R}$,$b^{*,R}$) represent the CIELAB coordinates of the paint film prior to any UV exposure.

2.4. Results and discussion

Figs. 1 and 2 represent the variations of ΔE as functions of both pigments' volume filling fractions for the P_E and P_R series of samples respectively. They show general common patterns but the magnitude of the measured color change is different between the samples: the E-Latex offers better resistance to fading than R-Latex.

In the case of low values Yellow PVC (0–0.02), one observes very large changes in ΔE on irradiation when TiO₂ concentration is low. This is because there may be sufficient UV radiation to degrade all of the pigment, leading to a complete bleaching. If the yellow pigment concentration is kept low and TiO₂ PVC is progressively increased the ΔE decrease. Again, this is to be expected as the perceived measured reflected color is a combination of
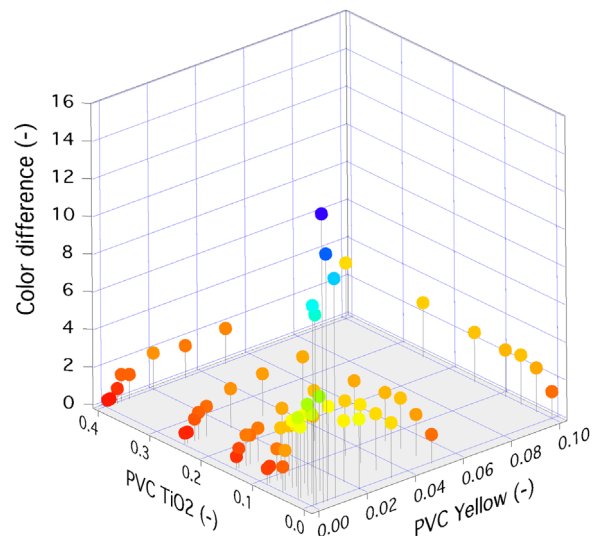

Fig. 1. Experimental data: color variations ΔE (CIE 1976) measured on the 63 samples dispersed in the E-Latex.